Novel filler and pigment

The present invention concerns a novel filler and pigment which can be used for producing paper, cardboard, polymers, paints, putties and similar products. In particular the invention concerns the use of calcium oxalate as a filler and/or a pigment in coated paper and cardboard having a predetermined brightness and opacity.

The invention also concerns a web of coated fibrous ~~material according to the preamble of claim 13~~.

Today, the trends of paper product development are to a growing extent decided by the buyers and by legislative measures.The buyers of printing papers want to save mailing costs and to cut the amount of waste generated. Waste management fees have also been imposed on packages, the amounts of which depend on the weight of the product. Generally, it appears that various energy and emissions taxes will have to be incorporated into the price of paper products, forming an extra cost load. For these reasons the paper buyers would like to have paper products of low grammage which, nevertheless, fill high quality standards. On the other, for the paper-based information distribution to be able to compete successfully with electronic media, it is required that the printing result of the paper products be further improved.

The above mentioned general trends put rather high requirements on the raw materials of the paper and on the manufacturing processes. Recently, in order to fulfil the requirements, extensive efforts have been made in order to improve the paper raw materials and the manufacturing processes thereof. It is an aim to manufacture high-quality papers by using smaller amounts of raw materials than before. When the grammage of the paper is reduced, the opacity of the paper become a critical feature. Opacity can be enhanced by increasing the filler content of the paper. This, however, reduces the strength of the paper and therefore efforts are being made to change the structure of the paper while still maintaining the important product properties. One additional property which is related to an increase of the filler and pigment amounts of paper and cardboard products is the increase of the

residual ash, which makes it more difficult to utilize recirculation fibers e.g. in energy production and to destroy them by burning, respectively. Furthermore the present mineral-based fillers and pigments cause great wear on the wire. This shortens the operational time of the wires.

It is an object of the present invention to remove the disadvantages of the prior art and to provide an entirely novel kind of solution for coating of papers and cardboards and for filling of papers, cardboards, polymers, paints and different pastes, putties and dispersions, in particular polymer dispersions. It is a particular aim of the present invention to provide a pigment and filler of papers and cardboards which makes it possible to lower the grammage without impairing the optical properties, in particular the opacity, of the paper. Further, according to the present invention novel kinds of paper and cardboard products are aimed at, said products having a reduce ash content and an improved heat/fire resistance.

The invention is based on the idea of using calcium oxalate, CaC_2O_4, as a filler and/or as a pigment. Calcium oxalate is practically insoluble in water at neutral and alkaline conditions. It is therefore suitable for use as a filler of paper and cardboard in modern paper making processes just as calcium carbonate. Furthermore, it has good optical properties which enable the use of it as a pigment in many products. The combustion residue of calcium oxalate is considerably much smaller than of conventional pigments and, according to the present invention, calcium oxalate can therefore be used for replacing at least a part of the conventional pigments and fillers needed for achieving a predetermined brightness and opacity of a paper or cardboard. Because the wear caused by the calcium oxalate is small it can be used e.g. in toothpastes and other pastes in which the filler is expected to cause a minimum of abrasion.

More specifically, the method of reducing the combustion residue of coated paper and cardboard exhibiting a predetermined brightness and opacity according to the present invention is characterized by what is stated in the characterizing part of claim 1.

The material web according to the invention is characterized by what is stated in the characterizing part of claim 13.

The present invention provides considerable advantages. Thus, as mentioned above, the optical effect of calcium oxalate is very good. Paper coated with this pigment has a good opacity and the surface weight thereof can be lowered. On the other hand the density of this pigment is smaller than that of conventional pigments which helps in reducing the grammage. According to the present invention sufficient opacity can be obtained by using less filler which gives the paper a better strength. By using calcium oxalate as a pigment and/or filler of paper, a lighter paper is obtained as a result, said paper having excellent optical properties.

Next, the invention will be examined more closely with the aid of the following detailed description and with reference to a number of working examples.

In the attached drawings, Figure 1 is an electron microscope image of calcium oxalate crystals and Figure 2 shows the particle size distribution of milled calcium oxalate.

The structure of calcium oxalate is

$$Ca(OOC)_2 \qquad (I)$$

Usually, it is present in hydrated form, having the brutto formula

$$CaC_2O_4 \times nH_2O \qquad (II)$$

wherein n is usually 1 or 2, generally 1 (monohydrate).

In Nature, it can be found in many plant cells and, e.g., in uroliths and kidney stones. As a pure substance it is generally classified as a laboratory chemical and it has been used for analytical purposes for determining calcium. Generally the oxalates have been found to have a lubricating effect as a metal coating (Encyclopedia of Chemical Technologyn, Third Edition, Kirk Othmer, Vol. 16, p. 630, John Wiley & Sons, New York). For oxalic acid there are a number of known uses, including treatment, cleaning and coating of metals. Also cleaning of textiles and coloring of various objects is known in the art.

According to SE Patent Application 8904337-7, calcium oxalate can be employed for reducing light-induced yellowing of wood-containing papers. However, said reference is silent about the use of calcium oxalate as a filler or pigment for reducing the combustion residue of papers and cardboards, in particular coated papers, having a predetermined brightness and opacity.

The present invention utilizes the finding that the light scattering coefficient of calcium oxalate in coating layers is very large (on the order of 250 to 500 m^2/kg, depending on the structure of the layer). We have found that the pigment packing is very optimal for the optical properties. In other word, although the refractive index is quite conventional the pigment provides a great light scattering index and, thus, great opacity potential. The value for the light scattering coefficient is very large compare even to titanium dioxide, which has a very large refractive index and for which the light scattering coefficient is on the order of 160 m^2/kg. As regards optical effect, the packing of the particules and, further, the structure of the coating are of central importance.

By using calcium oxalate as a pigment or filler it is possible to produce papers and cardboard having high opacity and/or brightness. In particular, by using calcium oxalate as the sole pigment and/or filler or as a part of the pigment/filler residue of papers or cardboards it is possible to obtain products having an ISO brigthness of 80 % or more, preferably 90 % or more. The opacity of the products can be increased to 80 % or more, preferably 90 % or more by using calcium oxalate as a filler/pigment.

In our tests we have further found that the wear caused by Ca-oxalate is very small compared to the wear caused by conventional pigments. This means that by adding it to coating colours instead of conventional pigments it will also be possible to decrease the wear of the wire.

Calcium oxalate has a very small solubility in water. Of the monohydrate only 0.0067 g/l dissolves in water at 13 °C and even at 95 °C only 0.014 g/l, which corresponds to the amount of calcium carbonate in calcite form dissolved at room temperature. The solubility of the dihydrate is even smaller. The solubility of gypsym is almost 500-times greater than

for calcium oxalate. By replacing a part of traditional fillers and pigments with calcium oxalate it is possible essentially to reduce the amount of soluble disturing substances at a paper mill.

Thermally, the calcium oxalate monohydrate is decomposed in three stages; first it releases evaporating (crystal) water, subsequently carbon monoxide is released and then carbon dioxide and finally calcium oxide is obtained. As a result of the thermal decomposition the weight of the calcium oxalate is reduced with 80 %. For this reason the amount of ash in paper and cardboard can be clearly reduced by replacing kaolin, gypsym or calcium carbonate with partially or entirely with calcium oxalate. This feature is also examined in Example 4 below. The combustion residue of papers and cardboards coated and/or filled with calcium oxalate can be as low as 50 %, preferably less, e.g. below 35 or 30 %, depending on the proportion of the calcium oxalate of the pigments and/or fillers of the product.

It should be pointed out that both water and carbon monoxide and carbon monoxide are capable of displacing air and oxygen and being incombustible gases in particular water and carbon dioxide clearly increase the heat and fire resistance of paper or cardboard. With the aid of the invention it is therefore possible to produce essentially fire-proof material webs.

Although the paper or cardboard material produced by the present invention is not easily (or spontaneously) ignited, it can still be discarded and distroyed by burning (combusting) it together with other flammable components, such as other paper and cardboard products or polymers etc. The present invention therefore provides for an advantageous method of discarding paper and cardboard products by combustion. The method comprises collecting used paper and/or cardboard products having a calcium oxalate content of at least 10 % of the dry matter and preferably at least 50 % of the total pigment/filler content of the products, combusting the paper and/or cardboard products, recovering the heat generated during combustion, and collecting and discarding the ash.

According to a preferred embodiment of the invention, a wood-containing or wood-free base paper can be provided for use in flame-proof wall papers. As known in the art, a wall

paper can be considered non-flammable if it contains, e.g. 15 % or less living fibre, whereas the balance is made up of rock (i.e. of mineral fillers/pigments), which is not easily combustible. According to the invention, the capability of calcium oxalate of releasing gases which displace oxygen can effectively be utilized, and calcium oxalate can therefore be used as an active fire retardent. Wall papers containing more than 85 % calcium carbonate (calculated from the dry weight) are at least essentially incombustible and they would probably also meet the coming SBI EU-standard, according to which a test specimen should resist a 70 cm propane flame having an effect of 40 kW/m^2.

As a filler, calcium oxalate is applied in amounts of about 0.1 to 90 %, preferably about 1 to 80 % of the dry matter, and as a pigment it can be applied at about 1 to 100 g/m^2 for each side of the web. Preferably the calcium oxalate proportion of the entire amount of pigments and fillers is about 10 to 100, in particular 10 to 95 %.

Calcium oxalate can be prepared by precipitation from oxalate solutions with calcium salts. It is also commercially available.

Precipitated calcium oxalate monohydrate has already as such a rather narrow particle size distribution, which can be further improved by milling. The average particle size of the precipitated product is about 3 µm, whereas the mediate size of ground calcium oxalate is about 1.2 µm. Over 90 % of the ground calcium oxalate particles are smaller than 2.3 µm, but only 10 % are smaller than 0.5 µm. This steep distribution provides good optical properties. The particle size distribution is examined in more detail in Example 1.

Figure 1 shows an electrone microscope picture of milled calcium oxalated crystals. The Figure also shows that the crystals are very much of equal size and about spherical.

For use as a filler precipitated calcium oxalate is suitable as such or milled.

The use of calcium oxalate as a filler and a pigment is described in the following in particular in connection with the manufacture of cellulosic products. It should however be pointed out that the same advantages and features, in particular the optical properties,

associated with these working example can effectively be utilized in many other fields of industry. Calcium oxalate can be employed as a filler in the polymer and paint industry and for the production of pastes and polymer dispersions. It is also conceivable that calcium oxalate can be used in cosmetic preparations, in pharmaceuticals (including toothpastes), in washing powders, fertilizers, etc.

The term "cellulosic material" denotes paper or board or a corresponding cellulose-containing material, which is derived from a lignocellulosic raw material, in particular from wood or from annual or perennial plants. Said material can be wood-containing or wood-free (LWC, SC, coated printing papers and fine papers) and it can be produced from mechanical, semi-mechanical (chemi-mechanical) or chemical pulp. The pulp can be bleached or unbleached. The material can also contain recycled fibers, in particular reclaimed paper or reclaimed board. Typically, the grammage of the material web lies in the range of 35 to 500 g/m^2.

Calcium oxalate is used as a filler of the cellulosic material in a manner known per se. Thus, a stock is formed from mechanical or chemical pulp by slushing the pulp into water. Filler is added in desired amount, typically 0.1 to 90 %, preferably about 1 to 70 %, calculated from the total weight of the web, the consistency of the stock being generally about 0.1 to 5 %. The aqueous phase of the stock comprises, for example, clarified filtrate of circulating water of the paper machinne. The pH of the pulp which is fed to the head-box is neutral or slightly alkaline. Typically the pH is about 6.5 to 8. The pH on the paper machine can be somewhat higher than of the dosing, typically about 6.8 to 8.5. If necessary, for adjusting the pH of the stock and for controlling the pH during paper making a suitable base or acid is used. The base comprises in particular an alkali metal bicarbonate or carbonate or alkali metal hydroxide. The acids used comprise mineral acids and acidic salts. Preferred acids comprise sulphuric acid and its acidic salts such as alum and the preferred base is sodium bicarbonate. The paper web is formed on a paper machine in a manner known per se.

Calcium oxalate can be formulated into suitable coating colours. In the present invention "coating colour" means a composition designed for the coating or surfacing of paper or

board, containing water and components known per se, such as pigments, binding agent and a component regulating the viscosity (a thickening agent). In addition to calcium oxalate, the following pigments can be used: calcium carbonate, calcium sulphate, aluminium silicate, kaolin (aluminium silicate containing cristallization water), aluminium hydroxide, magnesium silicate, talc (magnesium silicate containing cristallization water) titanium oxide and barium sulphate and mixtures of these. Also synthetic pigments may be employed. Primary pigments of those mentioned above are calcium oxalate, kaolin and/or calcium carbonate, usually amounting to over 50 % of the dry matter of the coating composition. Calcinated kaolin, titanium oxide, precipitated carbonate, satin white, aluminium hydroxide, sodium silica aluminate and plastic pigments are additional pigments and the amounts of these are usually below 25 % of the dry matter content of the mixture. Special pigments to be mentioned are special kaolins and calcium carbonates and barium sulphate and zinc oxide.

Any binding agent know per se, which is frequently used for manufacturing paper, can be used as a binder. In addition to individual binders it is also possible to use mixtures of binding agents. As specific examples of typical binding agents the following can be mentioned: synthetic latex-type binders consisting of polymers or copolymers of ethyleneically unsaturated compounds, such as butadiene-styrene type copolymers which can contain a comonomer with a carboxylic group, such as acrylic acid, itaconic acid or maleic acid, and poly(vinyl acetate) which contains comonomers having carboxylic groups. In combination with the afore-mentioned substances e.g. water-soluble polymers, starch, CMC, hydroxy ethyl cellulose and poly(vinyl alcohol) can be used as binders.

In the coating mixture there can further be used conventional additives and adjuvants, such as dispersing agents (e.g. sodium salt of poly(acrylic acid)), substances for adjusting the viscosity and water rentention of the mixture (e.g. CMC, hydroxyethyl cellulose, polyacrylates, alginates, benzoate), lubricating agents, hardeners for improving the water resistance, optical agents, anti-foaming agents and substances for regulating the pH and for preventing product degradation. The lubricating agents include sulphonated oils, esters, amines, calcium and ammonium stearates; the agents improving water resistance include glyoxal; optical agents include diaminostilben and derivatives of disulphonic acid; the anti-

foaming agents include phosphate esters, silicones, alcohols, ethers, vegetable oils, the pH-regulators include sodium hydroxide and ammonia; and, finally, the anti-degradation agents include formaldehyde, phenol and quaternary ammonium salts.

The coating compositions according to the present invention can be used both as pre-coat mixtures and as surface coating colours. For 100 parts by weight of pigment the coating colour typically contains about 0.1 to 10 parts by weight of the thickening agent and 1 to 20 parts by weight of a binder.

The composition of a typical pre-coat mixture is the following:

pigment/filler (calcium oxalate optionally together with some other pigment)	100 parts by weight
thickener	0.1 to 2.0 parts by weight
binder	1 to 20 parts by weight
additives	0.1 to 10 parts by weight
water	balance

The composition of a surface coating colour according to the present invention is, for example, the following:

pigment/filler I (calcium oxalate)	30 to 90 parts by weight
optionally a second pigment/filler II (e.g. fine kaolin and/or carbonate)	10 to 30 parts by weight
total pigment	100 parts by weight
thickener	0.1 to 2.0 parts by weight
binder	1 to 20 parts by weight
additives	0.1 to 10 parts by weight
water	balance

The amount of a coating applied on both sides of the web is typically about 5 to 100 g/m^2.

The opacity of papers coated with calcium oxalate pigments is generally over 95 % and an ISO brightness level of 92 % can be reached.

The following non-limiting examples illustrate the inveniton. The light scattering coefficients, light absorption coefficients and opacities have been determined by the standard SCAN 8:93. ISO brightness (R457) has been determined according to standard SCAN-P 3:93. The grammage of the sheets and their thicknesses are determined according to standards SCAN-P 6:75 and SCAN-P 7:75, respectively.

Example 1

Manufacture of a calcium oxalate product of pigment-quality and the particle size of the calcium oxalate

Calcium oxalate monohydrate powder ($CaC_2O_4xH_2O$) of laboratory quality was slurried in water. The slurry was milled in a ball mill with 1 mm glass pearls without additives. The milled material was drained with a ceramic filter and the particle size distribution of the product was assayed with a Coulter LS (cf. Figure 2). Numerically the particle size distribution was as follows:

Table 1. Pigment size distribution of milled calcium oxalate

% <	10	25	50	75	90
Size, µm	0.676	0.992	1.491	2.173	2.920

Thus, the particle size distribution of calcium oxalate is rather narrow which is beneficial for good optical properties.

The dry matter content of the product was 54 wt-% and the average particle size 1.4 µm.

Example 2

Determination of specific area and wearability of calcium oxalate

Using the milled slurry of Example 1 the wear caused on the wire and the specific area (BET) of Ca oxalate were determined.

The BET specific area of the sample was 4.4 m^2/g. The specific area of calcium oxalate was on the same order as for some PCC qualities.

The wearability of calcium oxalate was 2.79 g/m^2. In Table 2, calcium oxalate has been compared to traditional pigments.

Table 2. Wearability

Pigment	Wearability, g/m^2
ZnO, red lable	12.5
ZnO, gold lable	0.7
$CaCO_3$, HC90	36.2
PCC (skalenoedrical)	6.0
SPS kaolin	10.1
Talc	13.0
Calcium oxalate	2.49

As the table clearly shows, calcium oxalate causes clearly less wear on the wire than most of the conventional pigments.

Esimerkki 3

Determination of the optical properties of coating layers and of coated paper

The slurry of Example 1 was also subjected to determination of the light scattering and light absorption coefficients (Y and R475) of Ca oxalate. The determinations were made on both glass sheets and base paper. The optical properties determined comprised the S- and

K-values and the opacities. The values were determined at two different wave lengths (viz. 557 nm and 457 nm).

In order to determine the properties of the calcium oxalate film the pigment slurry was first applied on a glass sheet using a paste spreader with two different thicknesses of the layers.

From the films made on the glass sheets, R_o and R_∞ were first determined from the coated part. A piece of cardboard which had been coated with Ca oxalate slurry was used as background for the determination of the R_∞. For determining the thickness of the layer the thickness of the glass sheet was determined both for the coated and the uncoated parts. The surface area was determined by weighing the sheet and then by washing away the slurry film and weighing the sheet again.

The results of determining the surface areas, thicknesses and optical properties of the films made on the glass sheets are given in Table 3.

Table 3. Properties of calcium oxalate films made on glass sheets

Thickness of coating layer	95 µm	61 µm
557 nm		
Opacity, %	96.5	96.3
457 nm		
Light scattering coefficient, m^2/kg	360	430
Light absorption coefficient, m^2/kg	1.27	2.82
Opacity, %	98.4	95.7
ISO Brightness, %	91.9	89.2
Surface weight g/m^2	39.5	17.4
Thickness (coated), µm	1076	1041
Thickness (uncoated), µm	981	980

Next, the slurry was applied to a base paper containing mechanical pulp, having a surface weight of 47.0 g/m^2.

Corresponding measurements as above were made for the base paper and for combinations of base paper and pigment film. Since the s- and k-values can be considered additive properties, the presented results have been counted in such a way that the effect of the base has been substracted from the results obtained with the base + pigment film combination. The results are presented in Table 4.

Table 4. Properties of calcium oxalate layers made on base paper

Sample	Base paper, thickness 78 µm	Coated paper, thickness 92 µm
557 nm		
Opacity, %	86.2	93.4
457 nm		
Light scattering coefficient, m^2/kg	55.7	232
Light absorption coefficient, m^2/kg	2.19	0.46
Opacity, %	88.8	96.2
ISO brightness, %	75.6	82.2
Surface weight, g/m^2	47.0	13.2

In summary of the above-presented results it should be noted that the light scattering coefficient of calcium oxalate is very large and measured from a coating layer it is in the range of 250 to 500 m^2/kg depending on particle size and size distribution. The great value indicates that the packing of the pigments is very optimal for the optical properties. In other words, in spite of a refraction index of conventional magnitude (about 1.5 to 1.6) the pigment provides an extremely large light scattering coefficient and, thus, a great opacity potential. As regards opticial effect the packing of the particles and, further, the structure of the coating are very central features.

Example 4

The combustion residue of paper containing calcium oxalate was determined from the following laboratory sheets, having a mass of 1.63 g (dry):

Sheet 1 (reference): 40 wt-% kaolin; 60 wt-% fibers

Sheet 2 (reference): 40 wt-% calcium carbonate; 60 wt- % fibers

Sheet 3 40 wt-% calcium oxalate; 60 wt-% fibers.

The sheets were burnt and the combustion residues were measured by weighing.

The combustion residues were as follows:

Sheet 1:	0.65 g
Sheet 2:	0.46 g
Sheet 3:	0.25 g

Thus, the sheet containing calcium oxalate contained a clearly smaller residue after combustion than the sheet containing other pigments. This feature has a great importance for reducing the waste of the paper, which further diminishes costs at dump pits.